

Blending, Grafting, and Cross-Linking Processes between Poly(ethylene oxide) and a (4-Benzoylphenoxy)_{~0.5}(Methoxyethoxyethoxy)_{~0.5}Phosphazene Copolymer

Francesco Minto,[†] Mario Gleria,^{*,†} Alessandro Pegoretti,[‡] and Luca Fambri[‡]

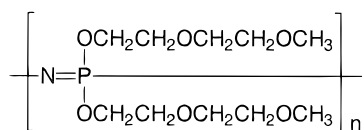
Istituto di Fotochimica e Radiazioni d'Alta Energia del C.N.R., Sezione di Legnaro, Via Romea 4, 35020 Legnaro, Padova, Italy, and Dipartimento di Ingegneria dei Materiali, Università di Trento, Via Mesiano 77, 38050 Mesiano, Trento, Italy

Received June 10, 1999; Revised Manuscript Received October 20, 1999

ABSTRACT: We report our results on the miscibility and irradiation of the blends of poly(ethylene oxide) (PEO) and a phosphazene copolymer almost equimolarly substituted with 4-benzoylphenoxy and methoxyethoxyethoxy moieties (BzMEEP). Differential scanning calorimetry (DSC) studies of the blends showed glass transitions temperatures (T_g) that increased regularly with the percentage of BzMEEP in the blend from about -50 °C up to -30 °C. Irradiation of these blends, under selected experimental conditions, leads to the absorption of the light by the benzophenone chromophore only in the copolymer, causing grafting of PEO onto the copolymer to occur concurrently with cross-linking reactions. Almost completely insoluble gellike materials were obtained. The percent of gel formed and degree of swelling of the cross-linked blends in chloroform were dependent on the amount of benzophenone, irradiation time, and molar mass of PEO.

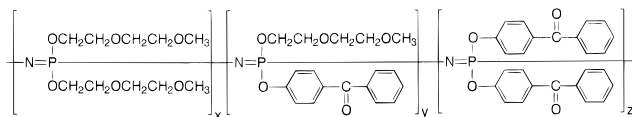
Introduction

The dimensional stability^{1,2} of poly[bis(methoxyethoxyethoxy)phosphazene],^{3,4} MEEP–POP,



is an intriguing problem in phosphazene chemistry that has been circumvented in the past following different strategies, i.e., UV,^{5,6} γ -rays,^{7–12} and chemical^{13,14} cross-linking, blend formation with crystalline poly(ethylene oxide) (PEO),^{1,15–18} and preparation of stable tridimensional networks with silica,^{19–26} titania, or zirconia,^{22,23,27–29} thus incorporating MEEP–POP particles into new ceramic materials.

We also looked to improve the dimensional stability of phosphazene polymers by preparing a new, highly photosensitive phosphazene copolymer that contained almost equimolar quantities of methoxyethoxyethoxy and 4-benzoylphenoxy substituents, BzMEEP,³⁰ having the following chemical structure:



where $x \approx y \approx z \approx 0.33$.

BzMEEP can form transparent thin films, is highly hydrophilic in nature due to the methoxyethoxyethoxy residues, and absorbs UV light because of the presence of the benzophenone chromophore. The overall photochemical behavior of BzMEEP in solid state, recently

investigated,³⁰ showed that (1) the polymer undergoes a 100% cross-linking process when irradiated for very short periods of time (2–3 s) with light of wavelength shorter than 370–380 nm to form a completely insoluble, dimensionally stable, cross-linked material; (2) the efficiency of this process and the degree of cross-linking can be reasonably controlled by finely tuning both irradiation time and excitation wavelength; and (3) the final cross-linked macromolecule very efficiently swells when immersed in water or in other solvents.

All these findings may be of considerable importance to favor the extensive utilization of MEEP–POP as an ionic conductor for the preparation of light batteries.^{1,6,13,31–33}

MEEP–POP and PEO have been reported to form blends over a large range of polymer compositions¹⁶ with significant improvement in dimensional stability as compared to the case of MEEP–POP.^{1,16,17,34,35} BzMEEP, like MEEP–POP and PEO, contains ethylene oxide units and, consequently, can also be expected to form blends with PEO.

If this is true, when blends between BzMEEP and PEO are formed, there should be a chemical interaction between the two partners that may result in the (a) partial or total miscibility of the polymers; (b) shifting of the T_g toward a unique value, intermediate between the starting glass transition temperatures of the original macromolecules; and (c) occurrence of photochemical events inside the BzMEEP/PEO systems upon irradiation.

The last fact is of particular importance because it may lead to the preparation of new types of phosphazene/PEO copolymers, potentially interesting in the ionic conductivity field, or as hydrogels for drug delivery systems.

In this paper, therefore, we report our findings on the thermal characterization of BzMEEP/PEO blends by differential scanning calorimetry (DSC) together with the photochemically induced grafting/cross-linking reactions in the blends.

[†] Istituto di Fotochimica e Radiazioni d'Alta Energia del C.N.R.

[‡] Università di Trento

* Corresponding author. E-mail gleria@lnl.infn.it.

Experimental Section

4-Hydroxybenzophenone, methoxyethoxyethanol, NaH 60% oil dispersion, and poly(ethylene oxide), PEO, of different molar mass were used as received from Aldrich. All the solvents used in this work for the preparation of BzMEEP (dioxane, toluene, xylene, ethanol, *n*-heptane, tetrahydrofuran) or for other manipulations (dichloromethane, chloroform, acetonitrile) were Carlo Erba analytical grade. When necessary, they were dried according to standard techniques.³⁶

Hexachlorocyclophosphazene, (NPCl₂)₃, was a Shin Nisso Kako product that contained small amounts of superior cyclophosphazene homologues (tetramers, etc.) and other impurities; for this reason it was purified by precipitation from hexane and successive vacuum sublimation until a constant melting point of 113 °C was reached.³⁷ This compound was successively polymerized by a thermal process (250 °C, 10⁻² Torr, for several hours) to produce poly(dichlorophosphazene),³⁸ a highly reactive polymeric precursor from which a phosphazene copolymer, BzMEEP, was prepared by nucleophilic replacement of the reactive chlorine with ethylene oxide and benzophenone moieties.³⁹⁻⁴¹ The synthesis and characterization of BzMEEP have been previously reported.³⁰

The preparation of films of PEO or of BzMEEP/PEO blends was achieved by casting from CH₂Cl₂ solutions of these polymers on Petri disks at a concentration of 10 or 20 mg/mL in dependence on high or low PEO molar mass, respectively.

The ultraviolet (UV) and infrared (IR) spectra of the BzMEEP and BzMEEP/PEO blends were determined using Perkin-Elmer spectrophotometers model 320 and 2000 Explorer, respectively.

Thermal characterization was performed by using a Mettler DSC 30 instrument with a heating rate of 10 °C/min in the range between -100 and +150 °C flushing nitrogen at 100 mL/min. A sample of pure indium was used to calibrate the measurements of temperature and enthalpy. By using a built-in Graphware TA72 program, the glass transition temperature, *T*_g, was determined as the inflection point of the thermogram, whereas the percentage of PEO crystallinity in the specimens was assessed by integrating the normalized area of the endothermic peak and rating the heat involved to the reference value of the 100% crystalline polymer (198 J/g).⁴²

The BzMEEP/PEO films were irradiated with a high-pressure mercury lamp (HBO, 150 W) using two series of cutoff filters in order to eliminate radiations of wavelength shorter than 250 or 350 nm. The polymer films (10 × 25 mm, with a thickness ranged between 40 and 200 μm) were supported onto an aluminum frame, put in a quartz flask, and irradiated under nitrogen atmosphere at 15 cm distance from the light source.

Both cross-linked BzMEEP and BzMEEP/PEO copolymers were characterized after irradiation by first determining the percentage of gel formed during the light exposure and successively measuring their swelling characteristics.

Gel fraction⁴³ was measured gravimetrically first by weighting irradiated samples of BzMEEP or BzMEEP/PEO systems, successively by immersing them in CH₂Cl₂ solutions in order to extract un-cross-linked part of the film, and eventually by weighting the dried extracted film, using the following formula:

$$\text{gel (\%)} = \frac{W_{\text{dry extracted film}}}{W_{\text{initial dry film}}^0} \times 100$$

The swelling degree at the equilibrium (*S*_{eq}) of the grafted BzMEEP/PEO copolymers after irradiation was determined gravimetrically, according to the following equation:⁴⁴

$$S_{\text{eq}} = \frac{W_{\text{swollen film}}}{W_{\text{initial dry film}}^0}$$

where *W*_{dry extracted film} is the weight of the BzMEEP/PEO blends extracted with CH₂Cl₂; *W*_{swollen film} is the weight of irradiated BzMEEP/PEO films swollen in CHCl₃ for 48 h, dried with

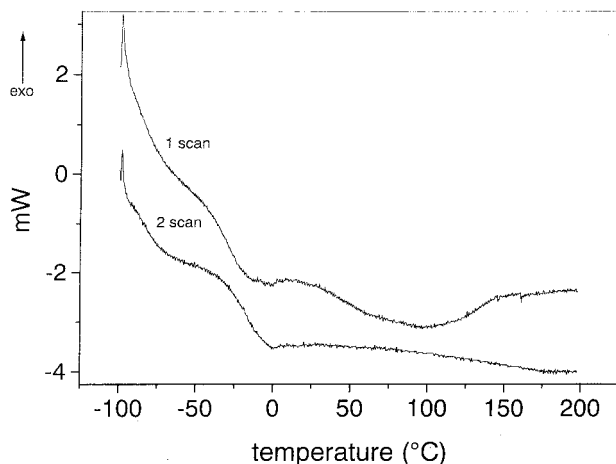


Figure 1. DSC thermograms of BzMEEP in two subsequent scans.

blotted paper, and weighted; and *W*_{initial dry film}⁰ is the weight of the dried film.

Results and Discussion

Thermal Characterization of the BzMEEP/PEO System. Films of BzMEEP were characterized by DSC measurements and the corresponding thermograms (first and second scans) of the polymer are reported in Figure 1. From these DSC data it appears that BzMEEP is an amorphous polymer with a hydrophilic character. In particular, the first scan shows a *T*_g at -27 °C and a broad endothermic peak in the range 30–180 °C, the latter mostly likely from evaporation of residual water (about 2%). In the second scan performed immediately after the first one, the dried polymer exhibited a slightly higher *T*_g (-20 °C) in the absence of the plasticizing effect of water (broad endothermic peak is absent). The same sample reanalyzed after 24 h of exposure to ambient conditions confirmed the hygroscopicity of BzMEEP because a thermogram similar to the initial one with *T*_g at -24 °C and the endothermic peak was found. Similar to the case of aryloxy-substituted polyphosphazenes,⁴⁵ the glass transition temperature of phosphazene copolymers containing mixed substituents falls within the range of *T*_g of the corresponding homo-substituted macromolecules, showing dependence on composition. By considering the Fox equation⁴⁶ for random copolymers

$$1/T_g = w_1(1/T_{g1}) + w_2(1/T_{g2}) \quad (I)$$

where *T*_{g1} and *T*_{g2} are the glass transition temperatures of the two components and *w*₁ = *w*₂ = 0.5 are their weight fractions, and by applying it to the case of the benzophenone/methoxyethoxyethoxy-substituted phosphazene copolymer, a *T*_g value of -32 °C was calculated for BzMEEP, comparable to the experimental value. For these calculations, thermal properties of the corresponding homopolymers containing methoxyethoxyethoxy units (MEEPPOP) or 4-benzoylphenoxy substituents (BzPOP) were considered. In fact, MEEPPOP is an amorphous polymer with very low *T*_g, -84 °C,⁴⁷ whereas BzPOP is a semicrystalline material with *T*_g of +61 °C, melting temperature of 180 °C, and enthalpy of 14 J/g.⁴⁸ The absence of a melting endotherm for BzMEEP is probably due to the inhibition of crystallization by the presence of a second substituent and the random structure of the copolymer.

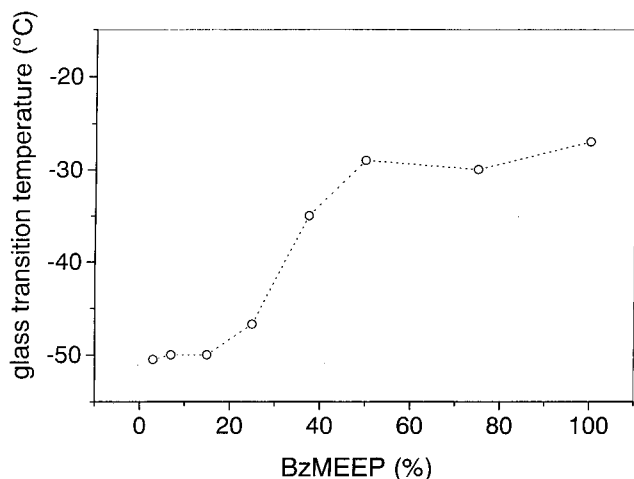


Figure 2. Glass transition temperature of BzMEEP/PEO blends (MW PEO = 1×10^5) evaluated as inflection point of the DSC thermogram.

In the case of BzMEEP/PEO blend, the glass transition temperature was determined by DSC measurements on films cast from CH_2Cl_2 solution. In these conditions, the crystallization of PEO with molar mass of 1×10^5 Da was measured very close to 100%, and in some cases the determination of T_g in these crystalline blends was made difficult because the signal was almost indistinguishable from the baseline noise.

Moreover, no T_g signal in the case of the PEO film was found by DSC analysis in the temperature range reported in the literature (-55^{49} to -44 °C⁵⁰). The dependence of T_g on the blend composition appears as a sigmoidal curve from -50 °C for low phosphazene content (3–15%) to about -30 °C for phosphazene percentages higher than 45%, as depicted in Figure 2.

In the case of the 3% and 7% BzMEEP blends, in order to overcome the signal/noise problem, two different runs were performed, and average T_g values of -50 ± 2 °C were determined for both systems.

Glass transition temperature values seem to indicate the formation of an amorphous PEO-rich phase and a BzMEEP-rich phase at low and high phosphazene percentage, respectively. Hence, partially miscible blends of crystalline PEO phase and amorphous PEO- or BzMEEP-rich phase were obtained, because only single T_g was observed for each blend sample. Moreover, as expected, the PEO phase always exhibited a melting peak at about 70 °C, whose intensity was dependent on composition. Other results with more sensitive techniques would have been required for T_g determination and phase analysis, such as dynamical mechanical thermal analysis.^{51–53}

Photochemistry of the BzMEEP/PEO System.

The thermal analysis by DSC of the BzMEEP/PEO blends showed that partially miscible blends are formed between these two macromolecules in a large range of compositions, which suggests the presence of specific interactions between the phosphazene copolymer and the poly(ethylene oxide) macromolecule. The proximity of BzMEEP and PEO components to each other in the blends, as implied by the miscibility in the amorphous phase, is a very important factor for the grafting and cross-linking reactions between the two components upon irradiation of the blends. On the contrary, efficient photochemical reactions between the two polymers in the blends are not possible if the two partners in the mixture are physically segregated in different micro-

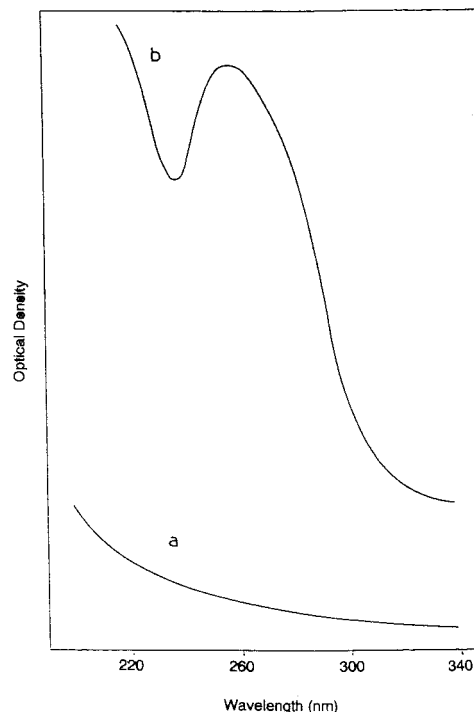


Figure 3. Optical density of PEO (a) and BzMEEP (1.2%)/PEO (b) films with thickness of 40 μm .

domains. This was the case, for instance, of the photochemistry of poly[bis(4-isopropylphenoxy)phosphazene], PiPP, sensitized by the benzophenone units present in poly[bis(4-benzoylphenoxy)phosphazene], BzPOP.⁵⁴

The spectroscopic characterizations of films (40 μm thick) of virgin PEO and of the BzMEEP/PEO system are reported in Figure 3.

As shown in this figure, the films of PEO have practically no absorption in the spectral range between 220 and 340 nm (curve "a"), the closest spectroscopic transition known for the polymer (i.e., $n-\sigma^*$) being located at 190 nm.⁵⁵ The corresponding absorption spectrum of the BzMEEP (1.2%)/PEO (98.8%) w/w films, same thickness as the PEO film, is also reported in Figure 3 (curve "b"), from which it appears that the $\pi-\pi^*$ transition of the benzophenone groups is responsible for the strong absorption located between 230 and 300 nm (λ_{max} 260 nm). Therefore, irradiation of the BzMEEP/PEO blends using light of wavelength longer than 250 nm (by cutoff filters) implies that the impinging light is completely absorbed by the benzophenone residue of the BzMEEP copolymer and that the corresponding photochemical behavior is basically determined by the benzophenone photoreactivity.

With increasing irradiation times, BzMEEP/PEO blends show a progressively smaller absorption of the band located at 260 nm (compare "a", "b", and "c" scans in Figure 4) and a concurrent increase in the absorption at wavelengths longer than 300 nm.

This spectroscopic behavior indicated that the benzophenone units of the BzMEEP copolymers are consumed during irradiation, possibly due to the onset of hydrogen abstraction reactions from the ethylene oxide groups of both BzMEEP and PEO macromolecules, forming ketyl radicals on the chromophore and highly reactive ethylene oxide radicals on both BzMEEP and PEO.

IR spectroscopy provides more information on the changes that occur upon irradiation.

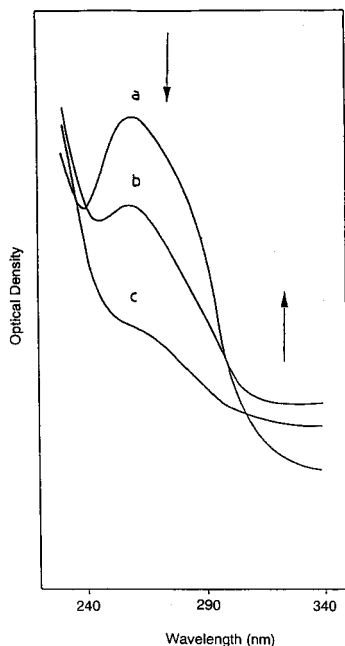


Figure 4. Optical density of BzMEEP (1.2%)/PEO films after 0 (a), 5 (b), and 30 min (c) of irradiation.

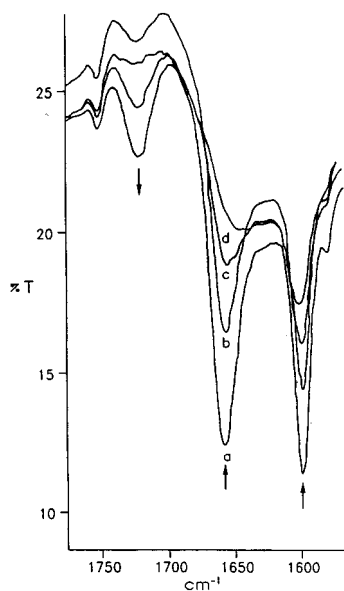


Figure 5. IR spectrum of BzMEEP (3%)/PEO films after 0 (a), 5 (b), 20 (c), and 60 min (d) of irradiation.

In Figure 5 the bands at 1600 and 1660 cm^{-1} represent the stretching vibrations of the aromatic ring and of the carbonylic group of the benzophenone moiety,⁵⁶ respectively. Both decrease with increasing irradiation times, while new bands are observed between 1700 and 1850 cm^{-1} . These facts indicate that the benzophenone units disappeared during illumination to form a variety of new, not well-defined, carbonyl species.

Moreover, the reaction of the ketyl radicals with other radical species present in the system may lead to the formation of LATs (light-absorbing transients)⁵⁷ that are responsible for the increase of the optical density in the spectral range above 340 nm (see Figure 4).

The formation of ethylene oxide radicals in both PEO and BzMEEP components of the blends, from hydrogen abstraction reactions from nearby excited benzophenone groups, is significant because these radicals can combine

intermolecularly, leading to cross-linking and grafting processes in the blends and formation of insoluble materials. The sequence of events proposed for these radical reactions is outlined in Scheme 1. Part "A" describes the light-induced hydrogen abstraction reactions by the excited benzophenone units of BzMEEP for both PEO and BzMEEP macromolecules, with the formation of the macroradical intermediates P^{\cdot} , R^{\cdot} , and R'^{\cdot} . Part "B" shows the reactions of radical species that could lead to cross-linking and grafting in the blends.

It should be pointed out that (1) the irradiation of PEO films only, under experimental conditions comparable to those adopted for the photolysis of the BzPOP/PEO systems, results in a totally unaffected polymer that does not change either solubility or molar mass; (2) on the other hand, BzMEEP film showed a slight increase of T_g from -27 to -16 $^{\circ}\text{C}$ after irradiation due to cross-linking of the polymer; (3) after irradiation of the BzMEEP/PEO blends and the successive deep washing of the resulting insoluble materials with $\text{CH}_2\text{-Cl}_2$, no BzMEEP could be detected in the recovered solvents, indicating that this macromolecule is always incorporated into the BzMEEP/PEO grafted copolymers due to the direct formation of radical species upon irradiation of these materials. Hence, the relative percentage of BzMEEP in the residual insoluble blend was always found to increase due to the fact that PEO macromolecules not grafted or cross-linked were removed after extraction.

Thermal analysis of BzMEEP/PEO blends after irradiation and solvent extraction showed T_g only for samples that had a substantial initial amount of BzMEEP (50 and 75%). The T_g of these BzMEEP/PEO blends, irradiated 30 min and extracted with solvents to give samples now containing 67 and 90% of BzMEEP, were found at -23 and -22 $^{\circ}\text{C}$, respectively. These values resulted about 8 deg higher than the values of the corresponding blends before irradiation, as the result of the cross-linking process of the polymers, similar to the case of pure BzMEEP. In the same time the residual grafted or cross-linked PEO in the blend after irradiation of 30 min and extraction with solvent exhibited a melting peak slightly lower than that present in not irradiated blends of equal composition.

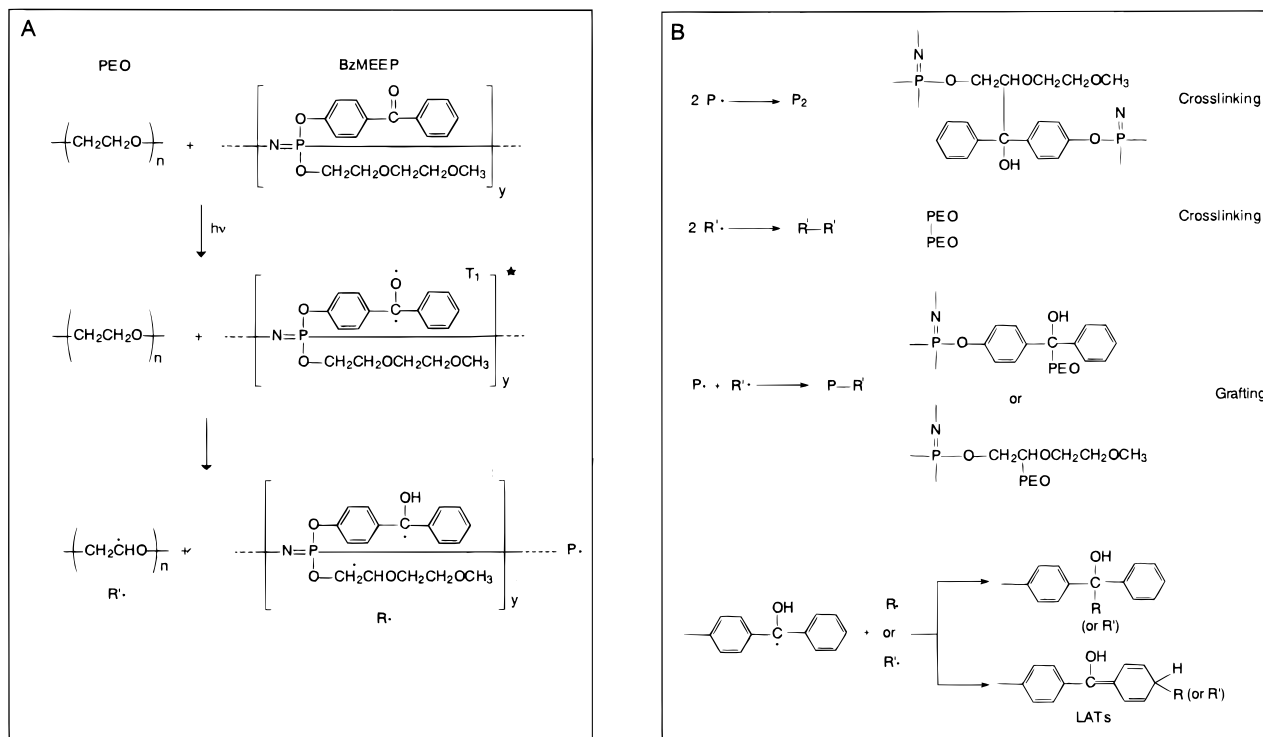
The effect of the irradiation time on the percentage of insoluble materials produced during photolysis is reported in Figure 6A for experiments involving a PEO of molar mass of 1×10^5 Da and using different percentages of BzMEEP in the original blend.

As shown in Figure 6A, the percentage of insoluble material increases steeply from the first minute of light exposure, and the kinetics of cross-linking could be evaluated in this interval after definition of the initial cross-linking rate as the slope of the best fit line, analogous to the light-induced polyphosphazene grafting.⁵²

From experimental results of blends with PEO of MW equal to 1×10^5 at different percentage of BzMEEP, we can now define a gel formation rate, GFR, expressed in %/min, that formally represents the amount of cross-linked blend in g per 100 g of initial blend after 1 min. This initial grafting rate can be determined as the slope of the best fit linear regression of the initial part of the diagram gel fraction, gel (%), vs time, at a certain BzMEEP percentage.

For different initial BzMEEP percentages of 1.2, 3, and 12.9% and PEO with the molar mass of 1×10^5 ,

Scheme 1



initial gel formation rates of 18 ± 4 , 25 ± 6 , and $40 \pm 11\%$ /min were evaluated, respectively. The reported errors derived from the error in the determination of the slope and the grafting rate were assumed zero for 0% of initiator. These data could be very well fit from the eq II

$$\text{GFR}_{\text{init}} = k_1[\text{BzMEEP}]^{1/2} - k_2[\text{BzMEEP}] \quad (\text{II})$$

where $[\text{BzMEEP}]$ represents the BzMEEP concentration expressed in percentage by weight. The constants $k_1 = 17.9 \pm 0.9\%^{1/2} \text{ min}^{-1}$ and $k_2 = 1.9 \pm 0.2 \text{ min}^{-1}$ formally account for a mechanism of radical formation and radicals recombination (cross-linking) or disproportionation in the initial stages of the reaction. In fact, two radical species could be formed after irradiation of a BzMEEP unit according to Scheme 1A, and hence the grafting rate is dependent on the square root of the concentration of BzMEEP that plays a similar role of the initiator in polymerization reactions.⁵⁸ On the other hand, the second term of eq II represents the disappearance of radical species that do not contribute to the grafting process due to the formation of cross-linked BzMEEP (Scheme 1B) or disproportionation products through-out a bimolecular radical reaction, depending on the first order of BzMEEP concentration.

However, the rate of this process decreases rapidly with the irradiation time in such a way that the formation of gel increases very slowly for periods of irradiation up to 60 min. The percent gel formed is directly related to the amount of benzophenone chromophore found in the blends, with higher amount of the latter corresponding to larger quantities of the insoluble materials obtained upon irradiation of BzMEEP/PEO blends. Quasi-plateau values of about 23, 35, and 50% were reached after 60 min of irradiation for film containing 1.2, 3, and 12.9% of BzMEEP, respectively.

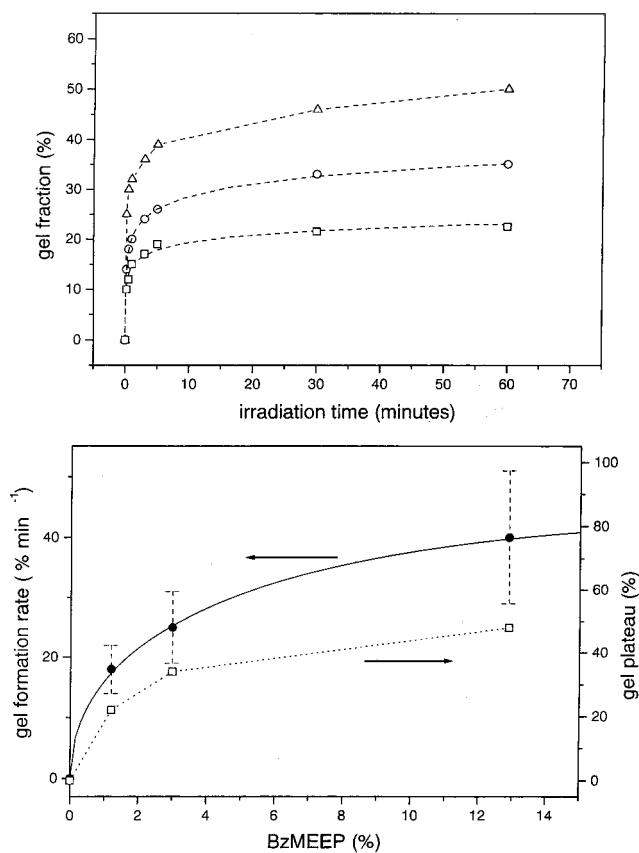


Figure 6. (A, top) Gel fraction of BzMEEP/PEO blends as a function of irradiation time. BzMEEP percentages of 1.2% (□), 3% (○), and 12.9% (△) in the blend and PEO with molar mass of 1×10^5 . (B, bottom) Gel formation rate of BzMEEP/PEO blend (●) and gel plateau value (□) as a function of BzMEEP percentage with PEO of molar mass 1×10^5 after 30 min of irradiation. The continuous line represents eq II.

Figure 6B shows that both the gel formation rate and

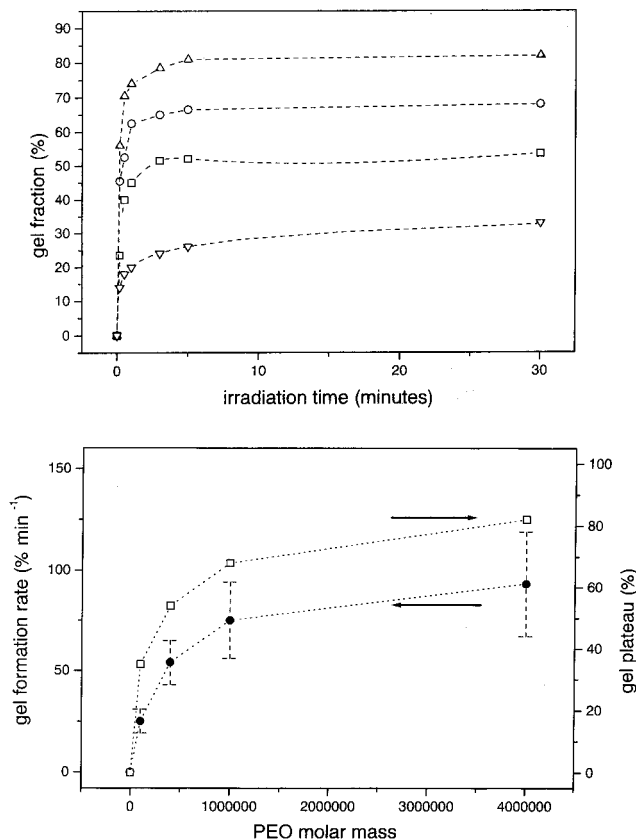


Figure 7. (A, top) Gel fraction of BzMEEP (3%)/PEO blends as a function of irradiation time with different PEO molar mass: 1×10^5 (∇), 4×10^5 (\square), 1×10^6 (\circ) and 4×10^6 (\triangle). (B, bottom) Gel formation rate (\bullet) and gel plateau value (\square) of BzMEEP (3%)/PEO blends as a function of PEO molar mass.

the gel fraction plateau increase with the BzMEEP percentage.

The efficiency of the formation of these grafted insoluble materials between BzMEEP and PEO is clearly related also to the molar mass of the PEO macromolecule blended with 3% BzMEEP and irradiated, as reported in Figure 7A.

All four samples containing different molar masses of PEO showed the same sigmoidal trend when percent gel was plotted versus irradiation time, although at different efficiencies. Blends using PEO molar masses of 1×10^5 , 4×10^5 , 1×10^6 , and 4×10^6 Da in an initial 3% BzMEEP composition gave initial gel formation rates of 25 ± 6 , 54 ± 11 , 75 ± 19 , and $93 \pm 26\%$ /min, respectively. The absolute amount of the insoluble BzMEEP/poly(ethylene oxide) mixture upon irradiation increases going from $\sim 25\%$ for PEO of 1×10^5 Da up to $\sim 80\%$ with PEO of 4×10^6 Da. Both the gel formation rate and the gel fraction plateau increase with the molar mass of PEO as shown in Figure 7B.

In Figure 8, the percentage of the insoluble BzMEEP/PEO copolymers is reported versus the molar mass of the poly(ethylene oxide) used during the light-induced insolubilization reaction with 3% of BzMEEP and 30 min of irradiation. Percent of gel formed increases steeply with larger molar masses of PEO, reaching almost 80% for a PEO of 4×10^6 Da. To obtain 100% of gel formation, according to these experimental results, an extrapolated value MW of about 13×10^6 Da can be estimated.

The direct consequence of the fact that large amounts of PEO are linked to the BzMEEP polymer is reflected

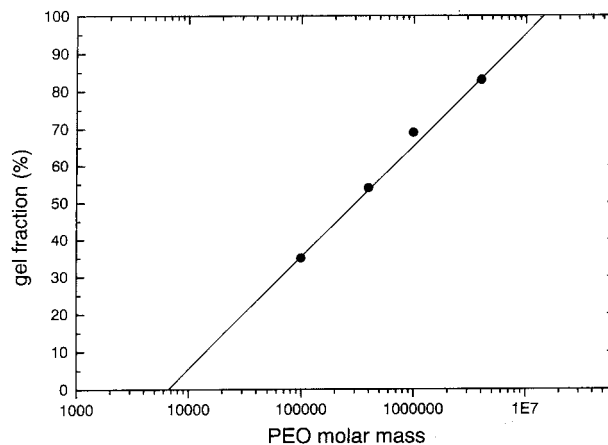


Figure 8. Gel fraction of BzMEEP (3%)/PEO after 30 min of irradiation as a function of PEO molar mass (1×10^5 , 4×10^5 , 1×10^6 , and 4×10^6).

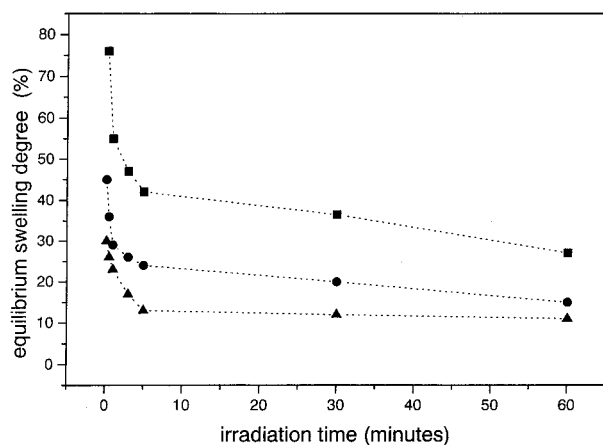


Figure 9. Equilibrium swelling degree of BzMEEP/PEO blends as a function of irradiation time. Initial BzMEEP percentages of 1.2% (\blacksquare), 3% (\bullet), and 12.9% (\blacktriangle) and PEO with molar mass of 1×10^5 .

in the increased hydrophilicity of these new materials and in the strong enhancement of their swelling capability in the presence of organic solvents or water.

In Figure 9 the equilibrium swelling S_{eq} of the insoluble BzMEEP/PEO copolymers in CHCl_3 is reported versus the irradiation time for three different irradiated blends containing 1.2, 3, and 12.9% w/w of BzMEEP, respectively. The S_{eq} is very high for short irradiation times (1–2 min), but it immediately decreases as soon as the irradiation time is increased up to 60 min of light exposure. Furthermore, the highest swelling effect is obtained for BzMEEP/PEO blends that contain the lowest amount of benzophenone groups. These facts strongly suggest that the degree of cross-linking of the irradiated BzMEEP/PEO mixtures is the factor dominating the swelling capability of these materials. Increased number of cross-links between the PEO and the BzMEEP chains (as obtained by using BzMEEP/PEO blends highly loaded with benzophenone residues or by longer irradiation times) is able to decrease the swelling efficiency of the irradiated samples.

The lowest S_{eq} values was obtained using 12.9% (w/w) of BzMEEP polymer in the blends, and with increasing irradiation times, the differences in the S_{eq} between the three samples become less.

In Figure 10 gel % (left) and S_{eq} (right) are plotted versus % of BzMEEP (i.e., of benzophenone photoiniti-

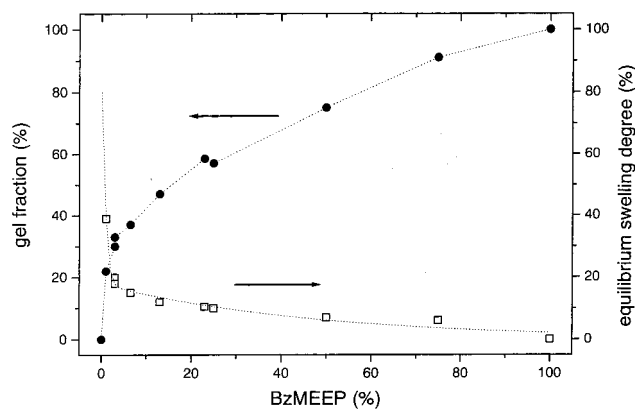


Figure 10. Gel fraction (●) and equilibrium swelling degree (□) of BzMEEP/PEO blends as a function of BzMEEP percentage with PEO of molar mass 1×10^5 after 30 min of irradiation.

ating species present in the BzMEEP/PEO system) (MW PEO = 1×10^5 Da; irradiation time 30 min). From this figure it appears quite clearly that an increase of the benzophenone photosensitizer in the reaction system brings about the increase in the PEO macromolecules that are linked to BzMEEP, which, in turn, is accompanied by a remarkable decrease in the swelling capability of this blend due to the extensive cross-linking present in these materials.

Conclusions

In this paper we reported the blend formation between poly(ethylene oxide) of variable molar mass and a phosphazene copolymer almost equimolecularly substituted with 4-benzoylphenoxy and methoxyethoxy-ethoxy moieties.

The phosphazene copolymer was found to form blends with PEO over a large range of polymer compositions as demonstrated by the shifting of the glass transition temperatures of the BzMEEP/PEO mixtures and proved to be extremely photosensitive due to the presence of benzophenone units attached to the phosphazene skeleton.

The selective excitation of the benzophenone chromophores in the BzMEEP/PEO blends by light of wavelength longer than 250 nm leads to grafting/cross-linking processes of the materials. The resulting insoluble species were characterized by DSC measurements, by spectroscopic techniques, and by swelling yield determinations.

It was shown that the degree of cross-linking of the irradiated system is directly related to the benzophenone content in the mixture, to the irradiation time, and to the molar mass of PEO used in this work; i.e., the more elevated the benzophenone concentration, the longer the irradiation time and the higher the molar mass of the PEO polymers, the higher the entity of the cross-linking, and the lower the swelling degree of the system.

References and Notes

- Abraham, K. M.; Alamgir, M. *Chem. Mater.* **1991**, *3*, 339.
- Allcock, H. R. In *Inorganic and Organometallic Polymers II. Advanced Materials and Intermediates*; Wisian-Neilson, P., Allcock, H. R., Wynne, K. J., Eds.; ACS Symposium Series: American Chemical Society: Washington, DC, 1994; Chapter 17, Vol. 572, p 208.
- Blonsky, P. M.; Shriver, D. F.; Austin, P. E.; Allcock, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 6854.
- Allcock, H. R.; Austin, P. E.; Neenan, T. X.; Sisko, J. T.; Blonsky, P. M.; Shriver, D. F. *Macromolecules* **1986**, *19*, 1508.
- Nelson, C. J.; Coggio, W. D.; Allcock, H. R. *Chem. Mater.* **1991**, *3*, 786.
- Allcock, H. R.; Nelson, C. J.; Coggio, W. D. U.S. US 5,414,025, 1995; *Chem. Abstr.* **1995**, *123*, 61305h, assigned to The Penn State Research Foundation.
- Allcock, H. R.; Fitzpatrick, R. J.; Gebura, M.; Kwon, S. *ACS Polym. Prepr.* **1987**, *28* (1), 321.
- Allcock, H. R.; Kwon, S.; Riding, G. H.; Fitzpatrick, R. J.; Bennett, J. L. *Biomaterials* **1988**, *9*, 509.
- Bennett, J. L.; Dembeck, A. A.; Allcock, H. R.; Heyen, B. J.; Shriver, D. F. *ACS Polym. Prepr.* **1989**, *30* (1), 437.
- Bennett, J. L.; Dembeck, A. A.; Allcock, H. R.; Heyen, B. J.; Shriver, D. F. *Chem. Mater.* **1989**, *1*, 14.
- Nazri, G. A.; Meibuhr, S. G. *J. Electrochem. Soc.* **1989**, *136*, 2450.
- Allcock, H. R.; Pucher, S. R.; Visscher, K. B. *Biomaterials* **1994**, *15*, 502.
- Tonge, K. M.; Shriver, D. F. *J. Electrochem. Soc.* **1987**, *134*, 269.
- Tonge, J. S.; Blonsky, P. M.; Shriver, D. F.; Allcock, H. R.; Austin, P. E.; Neenan, T. X.; Sisko, J. T. *Proc. Electrochem. Soc.* **1988**, *1*, 533.
- Semkow, K. W.; Sammells, A. S. *J. Electrochem. Soc.* **1987**, *136*, 766.
- Abraham, K. M.; Alamgir, M.; Reynolds, R. K. *J. Electrochem. Soc.* **1989**, *136*, 3576.
- Abraham, K. M.; Alamgir, M. U.S. US 5,166,009, 1992; *Chem. Abstr.* **1993**, *119*, 99857v, assigned to USA Secretary of the Navy.
- Subramony, J. A.; Kulkarni, A. R. *Solid State Ionics* **1994**, *67*, 235.
- Coltrain, B. K.; Ferrar, W. T.; Landry, C. J. T.; Molaire, T. R. *ACS Polym. Prepr.* **1991**, *32* (3), 477.
- Coltrain, B. K.; Ferrar, W. T.; Landry, C. J. U.S. US 5,010,128, 1991; *Chem. Abstr.* **1991**, *114*, 165903g, assigned to Eastman Kodak Co.
- Coltrain, B. K.; Ferrar, W. T.; Landry, C. J. T.; Molaire, T. R.; Zumbulyadis, N. *Chem. Mater.* **1992**, *4*, 358.
- Coltrain, B. K.; Ferrar, W. T.; Landry, C. J. T.; Molaire, T. R.; Schildkraut, D. E.; Smith, V. K. *ACS Polym. Prepr.* **1993**, *34* (1), 266.
- Ferrar, W. T.; Coltrain, B. K.; Landry, C. J. T.; Long, V. K.; Molaire, T. R.; Schildkraut, D. E. In *Inorganic and Organometallic Polymers II. Advanced Materials and Intermediates*; Wisian-Neilson, P., Allcock, H. R., Wynne, K. J., Eds.; ACS Symposium Series: American Chemical Society: Washington, DC, 1994; Chapter 20, Vol. 572, p 258.
- Guglielmi, M.; Brusatin, G.; Facchin, G.; Gleria, M.; De Jaeger, R.; Musiani, M. *J. Inorg. Organomet. Polym.* **1996**, *6*, 221.
- Brusatin, G.; Guglielmi, M.; De Jaeger, R.; Facchin, G.; Gleria, M.; Musiani, M. *J. Mater. Sci.* **1997**, *32*, 4415.
- Guglielmi, M.; Brusatin, G.; Facchin, G.; Gleria, M. *Appl. Organomet. Chem.* **1999**, *13*, 339.
- Landry, C. J. T.; Ferrar, W. T.; Coltrain, B. K. PCT Int. Appl. WO91 09,080, 1991; *Chem. Abstr.* **1991**, *115*, 234535y, assigned to Eastman Kodak Co.
- Landry, C. J. T.; Ferrar, W. T.; Coltrain, B. K. U.S. US 5,104,602, 1992; *Chem. Abstr.* **1991**, *115*, 234535y, assigned to Eastman Kodak Co.
- Landry, C. J. T.; Ferrar, W. T.; Coltrain, B. K. U.S. US 5,190,819, 1993, assigned to Eastman Kodak Co.
- Minto, F.; Gleria, M.; Bertani, Di Noto, V.; Vidali, M. *J. Inorg. Organomet. Polym.* **1998**, *8*, 67.
- Zurer, P. *Chem. Eng. News* **1984**, *62*, 23.
- Abraham, K. M.; Alamgir, M.; Perrotti, S. J. *J. Electrochem. Soc.* **1988**, *135*, 535.
- Nazri, G.; MacArthur, D. M.; Ogara, J. F. *Chem. Mater.* **1989**, *1*, 370.
- Abraham, K. M.; Alamgir, M.; Moulton, R. D. *J. Electrochem. Soc.* **1991**, *138*, 921.
- Abraham, K. M.; Alamgir, M.; Pasquariello, D. M. U.S. US 5,332,631, 1994; *Chem. Abstr.* **1994**, *121*, 160830r, assigned to E.I.C. Corp.
- Vogel, A. I. *A Textbook of Practical Organic Chemistry*; Longman: London, 1970.

- (37) Allcock, H. R. *Phosphorus-Nitrogen Compounds. Cyclic, Linear, and High Polymeric Systems*; Academic Press: New York, 1972.
- (38) De Jaeger, R.; Gleria, M. *Prog. Polym. Sci.* **1998**, *23*, 179.
- (39) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.
- (40) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.
- (41) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1716.
- (42) Van Krevelen, D. W. *Properties of Polymers*; Elsevier Scientific Publishing Co.: Amsterdam, The Netherlands, 1990.
- (43) Rabek, J. F. *Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers. Theory and Applications*; J. Wiley: Chichester, UK, 1987.
- (44) Doytcheva, M.; Dotcheva, D.; Stamenova, R.; Orahovats, A.; Tsvetanov, C.; Leder, J. *J. Appl. Polym. Sci.* **1997**, *64*, 2299.
- (45) Allcock, H. R.; Mang, M. N.; Dembek, A. A.; Wynne, K. J. *Macromolecules* **1989**, *22*, 4179.
- (46) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.
- (47) Allcock, H. R.; Visscher, K. B. *Chem. Mater.* **1992**, *4*, 1182.
- (48) Fambri, L., unpublished results.
- (49) Braun, D. B. In *Handbook of Water-Soluble Gums and Resins*; Davidson, R. L., Ed.; McGraw-Hill: New York, 1980; Chapter 19.
- (50) Harding, H. R.; Rose, J. K. In *Water Soluble Resins*; Davidson, R. L., Sittig, M., Eds.; Reinhold: New York, 1962; Chapter 10.
- (51) McCrum, N. G.; Read, B. E. *Anelastic and Dielectric Effects in Polymer Solids*; Dover Publications: New York, 1991.
- (52) Fambri, L.; Minto, F.; Gleria, M. *J. Inorg. Organomet. Polym.* **1996**, *6*, 195.
- (53) Fambri, L.; et al., manuscript in preparation.
- (54) Gleria, M.; Minto, F.; Bortolus, P.; Porzio, W.; Meille, S. V. *Eur. Polym. J.* **1990**, *26*, 315.
- (55) Sloop, S. E.; Lerner, M. M.; Stephens, T. S.; Tipton, A. L.; Paull, D. G.; Stenger-Smith, J. D. *J. Appl. Polym. Sci.* **1994**, *53*, 1563.
- (56) Silverstein, R. M.; Bassler, C. G.; Morrill, T. C. *Spectrophotometric Identification of Organic Compounds*; Wiley: New York, 1974.
- (57) Scaiano, J. C.; Abuin, E. B.; Steward, L. C. *J. Am. Chem. Soc.* **1982**, *104*, 5673.
- (58) Billmeyer, F. W. *A Textbook of Polymer Science*; Wiley: Singapore, 1984; p 56.

MA990922Q